



Electro-Chemical Devices

White Paper
**The Role of Alkalinity in Anaerobic
Wastewater Treatment Plants**

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Modern wastewater treatment plants must use a variety of physical, chemical and biological processes to implement effluent treatment best practice guidelines and to comply with regulations at the local, state and federal levels that protect the water supply. During treatment, these plants consume a variety of different chemicals. In some treatment plants, an alkali is used to provide the alkalinity level required to maintain effective biological activity and for pH control.

This article will discuss the role that alkalinity plays in wastewater treatment and how to monitor it during the process for effective treatment. First, it is important to define and discuss the term “alkalinity,” what it is and what it is not. Then it is necessary to understand that controlling alkali levels requires accurate effluent sample measurement in order to assure process safety, effectiveness and efficiency to manage costs.



Alkalinity: Definition and Composition

Alkalinity can be defined as the ability of a water to neutralize acid or to absorb

hydrogen ions. It is the sum of all acid neutralizing bases in the water. In municipal and industrial wastewater treatment processes, there are many factors that can contribute to alkalinity levels.

The factors that contribute to alkalinity levels in the process stream include:

- The type of dissolved inorganic and organic compounds present in the water
- The amount of suspended organic matter in the water
- Whether the water is strongly or weakly buffered
- The presence or absence of free hydroxyl alkalinity
- The amount of bicarbonate in the water
- The ratio of bicarbonate to dissolved carbon dioxide (CO_2), which is indirectly correlated to the amount of dissolved solids in the water

Knowing the relationship between alkalinity and pH levels in a wastewater process stream is important for effective treatment. The pH level is the measure of the hydrogen and hydroxyl ion concentration of the water, but it does not determine how many hydrogen ions that water can absorb. pH is a useful indicator of the transition between carbonate and bicarbonate alkalinity. pH is also used to determine the point at which alkalinity stops and free acidity begins. The pH of the water serves as a guide to the types of alkalinity present

in the water, but it is unrelated to the alkalinity content of a water sample.

The bacteria and other biological entities that play an active role in wastewater treatment are most effective at a neutral to slightly alkaline pH of 7 to 8. In order to maintain these optimal pH conditions for biological activity there must be sufficient alkalinity present in the wastewater to neutralize acids generated by the active biomass during waste treatment. This ability to maintain the proper pH in the wastewater as it undergoes treatment is the reason why alkalinity is so important to the wastewater industry.

The Problem

The standard test for alkalinity measures the quantity of acid neutralizing bases and represents this value in milligrams (mg) of CaCO_3 equivalents per liter (l) of wastewater. The term mg/l and the term ppm are used interchangeably in the wastewater industry. The amount of alkali that is added during waste treatment is determined by means of this standard test.

Various treatment plant operators will express the test results in different ways. Some operators will express the results in mg/l, some in ppm, some use pounds/gallon, others like the expression pounds per day while still others use the term pounds/million gallons.

This situation can be confusing at times because the industry uses different terminology to ask the same important question: How much alkalinity has to be added to the treatment system in order to neutralize acid and maintain the proper pH? The operator is looking for the number of gallons of magnesium hydroxide slurry or caustic soda that need to be added to the system on a daily or hourly basis.

Alkalinity and Treatment

In wastewater treatment processes, calcium and magnesium are essential elements that the bacteria need to carry on metabolic functions and reproduce. Other essential elements include nitrogen, phosphorus, potassium, iron, sulfur, oxygen, carbon and hydrogen. Without these elements present, the bacteria in treatment plants would not function properly, and this could result in an over-abundance of nuisance bacteria — the kinds that cause odors or inhibit settling.

We need some alkalinity to buffer against drops in pH values. Processes that biologically produce acids or acidic chemicals include:

- Biological nitrification (the conversion of ammonium to nitrite then nitrate)
- Anaerobic conditions in sewer systems
- Anaerobic conditions in primary clarifiers
- Anaerobic sludge digestion processes
- Anaerobic fermentation basins in biological phosphorus removal systems

- Chemical coagulant addition (aluminum sulfate, ferric sulfate, ferric chloride)
- Pure gaseous chlorine for disinfection

When these biological conditions occur in a treatment plant, or when acidic chemicals are added, the free hydrogen (H+) in the acid reacts with the negatively charged alkalinity, and the two effectively neutralize each other. If the water contained only the exact amount of alkalinity required to neutralize the acids, there would not be enough alkalinity remaining to protect the final pH value from falling if any additional acid were formed or added downstream.

Biological processes such as nitrification and anaerobic digestion rely on alkalinity. Without alkalinity, organic acids formed during these processes would drive the pH down to a point where the bacteria would be inhibited or could no longer survive.

For instance during the acid-formation stage of anaerobic digestion, volatile fatty acids are produced as acid-forming bacteria feed on the viscous, nearly septic sludge. A second group of bacteria, methanogens, then consume the volatile fatty acids. From this reaction, methanogens produce methane and bicarbonate alkalinity. The alkalinity they produce helps buffer the acid produced by the volatile acid formers.

The Solution

In a properly operated anaerobic digester, the ratio of volatile acid to alkalinity is

between 0.1 to 0.25 parts acid for every one-part alkalinity per liter. If a digester is overfed and volatile acids are rapidly increasing, the methane formers can't consume the acids fast enough. This causes the alkalinity to become depleted.

For example if the volatile acid climbs rapidly to 1,500 mg/L and the alkalinity is steady at 3,000 mg/L as CaCO₃, then the ratio becomes 0.5:1, and methane production slows down or even stops. If the operator does not take corrective action, the digester can become sour and stop working completely. In fact if the operator did not pay attention to alkalinity and used pH as the sole operating process control parameter, the digester could become sour before the pH finally indicated an operating problem.

Accurately and consistently measuring alkalinity helps maintain effective digester treatment of wastewater in both municipal and industrial systems. When specifying an alkalinity analyzer for this purpose, there are a number of factors to consider. These include:

- Accuracy
- Reliability
- Ease of installation
- Ease-of-use
- Maintenance requirements
- Initial cost
- Life-cycle costs

There are multiple alkalinity sensor options to explore: (1) titration and (2) colorimetric (methyl orange). Both measurement methods have their advantages and disadvantages depending on the site requirements, environment, etc.

The titration method of measuring total alkalinity requires the addition of small, precise quantities of sulfuric acid (the reagent) to the sample until the sample reaches a certain pH (known as an endpoint). The amount of acid used corresponds to the total alkalinity of the sample.

With the colorimetric method, the alkalinity is measured by the amount of standard sulfuric acid required to lower the pH of the water to a pH level of 4.5. This is indicated by the change in color of methyl orange from orange to pink.

There are multiple manufacturers who offer analyzers that use either method of measurement. Both methods are also acceptable to the U.S. Environmental Protection Agency (EPA) as suitable for the measurement of total alkalinity.

For example, the CA900 Alkalinity Titration Analyzer from Electro-Chemical Devices (ECD) provides real-time alkalinity measurement to ensure that the wastewater process has



the correct amount of alkalinity to ensure to the proper function of the wastewater system's anaerobic digester. The ECD CA900 complies with EPA method 310.1 for alkalinity by the mean of titrimetric analysis. When reviewing the previously recommended selection criteria for a total alkalinity analyzer, this device also meets all the recommended selection criteria.

In particular, the titration sensing method offers highly accurate, real-time results that allow plant operating teams to react quickly to situations where alkalinity levels could be dropping to undesirable levels that inhibit micro-organism activity in the digester tank. This ready-to-go analyzer is easy to set-up with its plug-n-play design and factory pre-calibrated sensor.

The analyzer's flexible design allows users



to select four separate measuring ranges: 0 to >1,000, 200 to 1,000, 50 to 200 and 0 to 50 ppm or mg/l. For operational ease, this analyzer comes with four 4-20 mA outputs and four configurable SPDT relays. It also includes an LCD display with touch-screen capability and web-enabled functionality. The lower cost and frequency of replacing titration analyzer reagents makes them more cost-effective to operate over time. With its two

compartment design that isolates its electronics from liquid sample analysis, it also minimizes maintenance.

Conclusions

Properly measuring alkalinity improves the effectiveness of wastewater treatment systems. Measuring pH alone is not

sufficient to determine alkalinity. When choosing an alkalinity analyzer, be sure to look at all the factors that will help determine the unit with the lowest life-cycle cost by looking beyond initial cost at maintenance costs and expected equipment life too.